

PAPERS ON
ETHERIFICATION
AND ON
THE CONSTITUTION OF SALTS

BY
ALEXANDER W. WILLIAMSON, LL.D., F.R.S.
(1850—1856)

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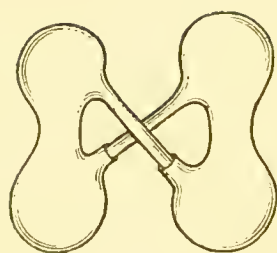
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PREFACE.

THE papers reprinted here form a group of great interest to the student of the historical progress of chemistry. They date from a period at which the development of synthetic organic chemistry was only beginning to occupy the attention of chemists to any considerable extent, and they deal with a number of questions which were matters of controversy at that period. The most important of these questions were undoubtedly those concerning the theory of etherification, and the true relationships of alcohol and ether to each other, and of both to water. It is in regard to his elucidation of these questions in particular that the name of their distinguished author, as that of one of the pioneers in the foundation of modern organic chemistry, will always be intimately connected with the history of chemistry.

In the cases of two papers which were communicated to meetings of The British Association, it has been considered advisable to reprint the short abstracts which appeared in the Reports of these meetings as

well as the full papers, which were published elsewhere.

It is a matter of much gratification to the Club that the reproduction of these papers is made during the life-time and with the consent of their author. For the kindly-expressed permission to reprint them, the Club returns grateful thanks to Dr Williamson.

L. D.

RESULTS OF A RESEARCH ON ÆTHERIFICATION.*

THE process by which this remarkable transformation of the elements of alcohol is effected has been the subject of much discussion among chemists ; of the two theories which have been devised to explain it, each counts among its supporters many first-rate chemists.

The facts upon which the contact theory lays peculiar stress are more physical than those to which the appropriately-designated chemical theory refers for its evidence. But there is one point upon which the two differ essentially, and that is the composition of alcohol ; the one maintaining that the two products, æther and water, are made from 2 atoms of alcohol ; the other, that they are both produced from 1 atom of double size. This is a difference of fact, and is therefore susceptible of being decided by experiment, as it requires nothing more than a direct evidence of the relative atomic weights of alcohol and æther.

An experiment was accordingly devised, of such a nature as to give a result according to the simple, differing from that according to the double atomic weight of alcohol. It consisted in making æther from alcohol by a new process, in which the various steps

* [From *Report of the Twentieth Meeting of the British Association for the Advancement of Science*, 1850, part 2, p. 65.]

of which it consists were performed separately. One-sixth of the hydrogen of alcohol was first expelled by the action of potassium; this compound differs from æther by having half as much carburetted hydrogen as that body to an equivalent weight of potassium to the other half, or by doubling its atomic weight, may be supposed to contain æther and potash. By double decomposition with iodide of æthyle, this substance was converted into æther, and not into a body of double the atomic weight of æther, which would have been the case according to the chemical theory of ætherification. By acting upon the same potassium compound with other iodides, new æthers were obtained, which to 1 atom of oxygen contained two different carburetted hydrogen atoms, one of which was contained in the alcohol, the other occupied the place of the hydrogen of that body.

In the common process of ætherification, sulphovinic acid is known to be the immediate product of the action of the sulphuric acid upon the alcohol. Now this sulphovinic acid is strictly analogous to iodide of æthyle and iodide of hydrogen. To convert alcohol into æther, it has merely to exchange its æthyle for the hydrogen, which in the preceding experiment was expelled by potassium. It is thus reconverted into sulphuric acid, to recommence a similar circle.

The continuous action of the reagent sulphuric acid, of which a given quantity is known to be capable of converting an unlimited amount of alcohol into æther and water, is thus owing to an exchange of analogous molecules in alternately opposite directions, and is distinctly different from any effect of chemical affinity.

THEORY OF ÆTHERIFICATION.* †

WHEN sulphuric acid is brought in contact with alcohol under certain circumstances, a new arrangement is effected in the elements of the alcohol, which divide into two groups, forming æther and water. Now it is well known that the process by which this change is effected may be represented in two ways, the difference of which consists in their respectively selecting for starting-point a different view of the constitution of alcohol. According to the one view, an atom of alcohol weighs 23, and is made up of C^2H^6O ; so that to form æther, two atoms of it are needed, one of which takes C^2H^4 from the other, setting free the water with which these elements were combined; whereas, according to the other view, alcohol weighs 46, and *contains* æther and water. These are not the only points of difference which are urged; but they are the most real and tangible, and their consideration is sufficient for our present purpose. If by any direct fact we could decide which of these two expressions is the correct one, the ground would be clear for an examination of the process of ætherification itself. In order to show more clearly the true meaning of the facts I have to adduce on this point, I will bring them before you in the order in which they arose.

My object in commencing the experiments was to obtain new alcohols by substituting carburetted hydro-

* [From *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, [3] vol. xxxvii., (1850), pp. 350-356.]

† Communicated by the Author; having been read before the British Association at Edinburgh August 3, 1850.

gen for hydrogen in a known alcohol. With this view I had recourse to an expedient, which may render valuable services on similar occasions. It consisted in replacing the hydrogen first by potassium, and acting upon the compound thus formed by the chloride or iodide of the carburetted hydrogen which was to be introduced in the place of that hydrogen. I commenced with common alcohol, which, after careful purification, was saturated with potassium, and as soon as the action had ceased, mixed with a portion of iodide of æthyle equivalent to the potassium used. Iodide of potassium was readily formed on the application of a gentle heat, and the desired substitution was effected ; but, to my astonishment, the compound thus formed had none of the properties of an alcohol—it was nothing else than common æther, $C^4H^{10}O$.

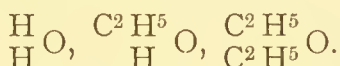
Now this result at once struck me as being inconsistent with the higher formula of alcohol ; for if that body contained twice as many atoms of oxygen as are in æther, I ought clearly to have obtained a product containing twice as much oxygen as æther does. The alternative was evident ; for having obtained æther by substituting C^2H^5 for H in alcohol, the relative composition of the two bodies is represented *by expressing that fact in our formula*. Thus

alcohol is $\begin{smallmatrix} C^2H^5 \\ H \end{smallmatrix} O$, and the potassium compound is $\begin{smallmatrix} C^2H^5 \\ K \end{smallmatrix} O$; and by acting upon this by iodide of æthyle,

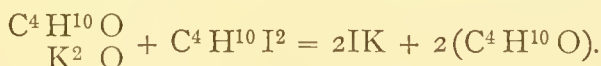
we have $\begin{smallmatrix} C^2H^5 \\ K \end{smallmatrix} O + C^2H^5I = IK + \begin{smallmatrix} C^2H^5 \\ C^2H^5 \end{smallmatrix} O$.

Of course the proportion between the two bodies is the only point upon which I here enter, and the same reasoning would be applicable to any multiple of the formulæ assumed. Some chemists may per-

haps prefer doubling them in order to avoid the use of atoms of hydrogen, potassium, &c.; but I have not felt myself justified in doing so, because that would involve doubling the usual formula for water; for, as I will presently show, water is formed in ætherification by replacing the carburetted hydrogen of alcohol by hydrogen, which, of course, obliges us to assume the same unity of oxygen in both. Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and æther is water in which both atoms of hydrogen are replaced by carburetted hydrogen: thus,



This formation of æther might however be explained after a fashion by the other theory — by supposing the potassium compound to contain æther and potash, which separate during the action of the iodide of æthyle; so that half the æther obtained would have been contained in that compound, and the other half formed by double decomposition between potash and iodide of æthyle: thus—



But although the insufficiency of this explanation becomes evident on a little reflection, I devised a further and more tangible method of arriving at a conclusion. It consisted in acting upon the potassium compound by iodide of methyle, in which case I should, if that compound were æther and potash, obtain a mixture of æther and oxide of methyle; whereas in the contrary case I should obtain a body of the composition $\text{C}^3\text{H}^8\text{O}$. Now this substance I obtained, and neither æther nor oxide of methyle.

In this experiment the two theories cross one another, and must lead to different results ; for it is evident that, in the first-mentioned decomposition by which æther was formed, the only difficulty in explaining the process decisively consisted in our inability to prove that the carburetted hydrogen introduced instead of the hydrogen did not have in the product an atom of oxygen to itself, but that, on the contrary, it was coupled with the carburetted hydrogen already contained in the alcohol—the two in combination with one atom of oxygen. It is clear that if alcohol *contain* æther and water, and the carburetted hydrogen in my first experiment formed a second atom of æther by taking the place of the hydrogen of this water, that the process being the same in the second experiment, we should then have obtained two æthers. Whereas if the formation of æther from alcohol be effected by synthesis, a new carburetted hydrogen being added to the one already contained in the alcohol, we ought to obtain the new intermediate æther which I obtained.

The complete description of this remarkable body and of its decompositions, will form the subject of a future paper. I will now merely state that its boiling-point is a little above 10° Cent. ; it is possessed of a very peculiar smell, distinctly different from that of common æther ; and, like that body, it is only slightly soluble in water. It is not acted upon by the alkali-metals at the common atmospheric temperature.

By acting upon the potassium-alcohol in like manner by iodide of amyle, I effected a similar substitution of the elements of that carburetted hydrogen in the place of the hydrogen of alcohol, and obtained an æther boiling at 111° C., having the composition $C^7H^{16}O$. There is some reason to believe that this

body is the same which Balard obtained by decomposition of chloride of amyle by an alcoholic solution of hydrated potash, and which that distinguished chemist took for oxide of amyle.

From the perfect analogy of properties between the known terms of the alcoholic series, it was to be expected that similar substitutions might be effected in the others ; and I have verified this by experiment. Of course the formulæ of the other alcohols must be reduced to half, for the same reasons as that of common alcohol. Methylic alcohol is therefore expressed

by the formula $\frac{\text{CH}^3}{\text{H}} \text{O}$, as common alcohol is $\frac{\text{C}^2 \text{H}^5}{\text{H}} \text{O}$;

and in the same manner amylic alcohol is $\frac{\text{C}^5 \text{H}^{11}}{\text{H}} \text{O}$,

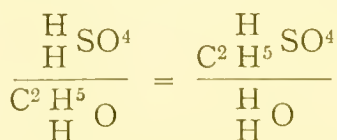
and the same of the higher ones. In conformity to this fact, we must be able to obtain the same intermediate æthers by replacing hydrogen in these alcohols (methylic and amylic) by the carburetted hydrogen of iodide of æthyle, as by the inverse process described above. This I have verified in the case of the three-carbon æther, which may be obtained indifferently by replacing one-fourth of the hydrogen of methylic alcohol by $\text{C}^2 \text{H}^5$, or by replacing one-sixth of the hydrogen of common alcohol by CH^3 .

Its rational formula is therefore $\frac{\text{C}^2 \text{H}^5}{\text{C} \text{H}^3} \text{O}$.

By acting upon the compound $\frac{\text{CH}^3}{\text{K}} \text{O}$ by iodide of amyle, I obtained a third æthereal compound, of which the formula is $\frac{\text{C} \text{H}^3}{\text{C}^5 \text{H}^{11}} \text{O}$. This is evidently the only one of the three new æthers, which, containing an even number of carbon atoms, might be conceived to have been formed from one alcohol ; but when

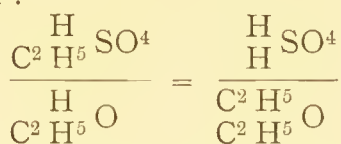
treated with monobasic acids, as hydrochloric, it cannot be expected to act in the same manner as its homogeneous isomeric, the æther $\frac{\text{C}^3 \text{H}^7}{\text{C}^3 \text{H}^7} \text{O}$ of the three-carbon alcohol $\frac{\text{C}^3 \text{H}^7}{\text{H}} \text{O}$; but of this I will give an exact account in the paper above alluded to.

My task is now to explain the process of ætherification by the action of sulphuric acid ($\text{SO}^4 \text{H}^2$) upon alcohol; and in order to accomplish that, I must show the connexion between those substances and the reagents used in the above-described experiments. With this view, I have merely to add to the above facts the acknowledged analogy of the simple and compound radicals in their compounds. I must first show how a substance analogous to my iodide of æthyle is formed, and then how by double decomposition with alcohol it produces æther. This is very easy; for sulphovinic acid is strictly analogous to iodide of æthyle plus iodide of hydrogen, which we should obtain by replacing SO^4 in its formula by an equivalent of iodine; and in order to represent the formation of this sulphovinic acid, which is well known to precede that of æther, the simplest mode is at the same time the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter: thus—



Now from this point it is clear that the process is the same as in the decompositions above described;

for by this sulphovinic acid coming in contact with an atom of alcohol, it reacts exactly in the same manner as the iodide did, forming of course sulphuric acid and æther :



The sulphuric acid thus reproduced comes again in contact with alcohol, forming sulphovinic acid, which reacts as before ; and so the process goes on continuously, as found in practice.

We thus see that the formation of æther from alcohol is neither a process of simple separation, nor one of mere synthesis ; but that it consists in the substitution of one molecule for another, and is effected by double decomposition between two compounds. I therefore admit the contact theory, inas-much as I acknowledge the circumstance of contact as a necessary *condition* of the reaction of the molecules upon one another. By reducing the formulæ of the alcohols to one atom of oxygen, I also retain the equality of volumes which the contact theory insists upon between the vapours of these bodies and their æthers, so that æther truly contains the elements of olefiant gas in addition to those of alcohol in one atom. But, on the other hand, I attach equal importance to all the essential facts of the chemical theory, and rest my explanation of the process as much upon them as upon those of the contact theory ; for, one-sixth of the hydrogen in alcohol truly exhibits different reactions from the remaining five, and must therefore be contained in that compound in a different manner from them ; and the alternate formation and decomposition of sulphovinic acid is

to me, as to the partisans of the chemical theory, the key to explaining the process of ætherification.

Innovations in science frequently gain ground *only* by displacing the conceptions which preceded them, and which served more or less directly as their foundation; but, if the view which I have here presented be considered a step in our understanding of the subject, I must beg leave to disclaim for it the title of innovation; for my conclusion consists in establishing the connexion and showing the compatibility of views which have hitherto been considered contrary; and the best possible justification of the eminent philosophers who advocated either one of the two contending theories, is thus afforded by my reconciling their arguments with those of their equally illustrious opponents.

Before quitting the subject of ætherification, I would wish to add a few words on an application which naturally enough suggests itself of the fact to which the process is here ascribed. I refer to the transfer of homologous molecules in alternately opposite directions, which, as I have endeavoured to show, is the cause of the continuous action of sulphuric acid in this remarkable process. It may naturally be asked, why do hydrogen and carburetted hydrogen thus continuously change places? It cannot be from any such circumstance as superior affinity of one molecule over another, for one moment sees reversed with a new molecule the transfer effected during the preceding one. Now in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged; that if hydrogen and amyle can replace one another in a compound, hydrogen and æthyle, which are

more nearly allied in composition and properties, must be able to replace one another more easily in the same compound ; and that the facility of interchange of hydrogen and methyle, which are still more similar, will be still greater. But if this be true, must not the exchange of one molecule for another of *identical* properties be the most easily effected of all ? Surely it must, if there be any difference at all ; and if so, the law of analogy forbids our imagining the fact to be peculiar to hydrogen among substances resembling it in other respects. We are thus forced to admit, that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition Cl H , the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course this change is not directly sensible to us, because one atom of hydrochloric acid is like another ; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place), the basilous elements hydrogen and copper do not limit their change of place to the circle of the atoms with which they were at first combined, the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid. Thus it is, that at any moment of time in which we examine

the mixture, the bases are divided between the acids ; and in certain cases, where the difference of properties of the analogous molecules is very great, it is found that the stronger acid and stronger base remain almost entirely together, leaving the weaker ones combined. This is well known in the case of a mixture of sulphuric acid and borax, and is a confirmation of our fundamental assumption, that the greater the difference of properties, the more difficult is the alternate interchange of one molecule for another.

But suppose now that instead of sulphate of copper, we mixed sulphate of silver with our hydrochloric acid in aqueous solution, and that a similar division of the bases between the acids established itself in the first moment, forming four compounds, SO^4H^2 , SO^4Ag^2 , ClH , ClAg ; it is clear that this last-mentioned compound, being insoluble in water, must, on its formation, separate out and remove from the circle of decompositions which solubility established. But of course the three compounds remaining in solution continue the exchange of their component parts, and give rise successively to new portions of chloride of silver, until as much of that compound is precipitated as the liquid contained equivalents of its component parts, a very small quantity remaining in solution and in the circle of decompositions.

Such is the general process of chemical decomposition. Of course a compound is removed as effectually from the circle of decompositions by possessing the gaseous form under the circumstances of the experiment, or even by being a liquid insoluble in the menstruum. I believe this explanation coincides in its second part with the one proposed many years ago by Berthollet ; but not making use of the

atomic hypothesis, upon which my explanation is based, that eminent philosopher went no farther back than the division of the acids between the bases on the mixture of salts, a fact which I have here deduced from the motion of atoms. It is well known that the general fact upon which Berthollet founded his view is denied by some eminent chemists of the present day ; but I believe the instances which they adduce are only apparent exceptions to the law, and will on further examination be found to afford additional confirmation of the truth of the great Savoy-sien's conception, as I have shown in the case of boracic and sulphuric acids.

In using the atomic theory, chemists have added to it of late years an unsafe, and, as I think, an unwarrantable hypothesis, namely that the atoms are in a state of rest. Now this hypothesis I discard, and reason upon the broader basis of atomic motion.

SUGGESTIONS FOR THE DYNAMICS OF CHEMISTRY DERIVED FROM THE THEORY OF ETHERIFICATION.*

THE human mind is only capable of understanding complicated phenomena when prepared by the study of simpler ones ; and one of the most remarkable illustrations of this necessary order is afforded by the preparation of dynamical laws by the consideration of statical facts. In statics we consider phenomena in a state of rest, while in dynamics we study their change ; and this distinction has been concisely stated by saying that the transition from the statical to the dynamical point of view, consists in superadding the consideration of *time* to that of space.

To represent the unknown cause of any change in phenomena, the word FORCE has been formed, and is generally retained until the law of that change has been discovered ; so that the dynamics of a subject may be said to constitute the explanation of the phenomena belonging to it.

It unfortunately often occurs that names are mistaken for explanations, and people deceive themselves with the belief that, for instance, in attributing chemical decompositions to affinity, attraction, contact-force, catalysis, &c., they explain them.

But owing to the necessary dependence of investigations on our mental operations, there is always a deficiency of facts corresponding to the imperfection

* [From *Notices of the Proceedings at the Meetings of the Members of the Royal Institution*, vol. i., 1851-1854, pp. 90-94.]

of theory ;—that is, we only seek and see those facts which are more or less connected with our theoretical notions, and in most cases shut our eyes to such cases as appear contrary to them. This is peculiarly the case with chemical theory and chemical facts at the present day ; for our atomic theory represents only certain simple and definite proportions of combination, and our researches have been fruitful in the investigation of such cases alone, the number of compounds of which we know nothing being infinite, compared to those definite ones which we have studied.

In fact, it is certain that if we could sufficiently disengage our minds from preconceived notions on the subject, we should view those substances, which, by more or less troublesome processes, we separate out from the bodies presented to us by nature, rather as exceptional and artificial products, than as the most normal and natural.

The lecturer submitted that the definite compounds hitherto exclusively acknowledged and studied by chemists, are in truth only exceptionally simple cases of combination, and that the consideration of chemists is only limited to them, because the atomic theory is as yet purely statical. The atomic theory has hitherto been tacitly connected with an unsafe and unjustifiable hypothesis, namely, that the atoms are in a state of rest ; the dynamics of chemistry will commence by the rejection of this supposition, and will study the degree and kind of motion which atoms possess, and reduce to this one fact the various phenomena of change, which are now attributed to occult forces. But although it will probably be generally used in connection with the atomic theory, the fact of motion is independent of any particular theory ; and however the properties of matter may be conceived, it will

remain true, that a change of place among the representatives or possessors of these properties, is constantly going on, which produces the phenomena of chemical combination.

Chemical science has proved the indestructibility of matter, but it has yet to prove the indestructibility of motion or momentum by showing its transfer and dispersion among atoms.

There are many *prima facie* evidences that *time* is necessary for chemical action:—but this fact, although it has been noticed, has not as yet entered into the explanation of phenomena.

The one instance in which a certain regular motion of the constituents of a mixture was first proved, is the process of etherification, of which the anomalous character has long since attracted the attention and study of many of the most eminent chemists, and has given rise to various theories which respectively represented part of the phenomena.

The lecturer referred to the importance of having a correct standard of comparison for the various chemical groups or molecules, and briefly alluded to the evidence afforded by the formation of the intermediate ethers, that alcohol and various bodies allied to it have of late years been incorrectly represented comparatively to metallic oxides and ethers, and that the weight of alcohol which is truly equivalent to ether or water, is not 46 but 23.

Having proved by a direct experiment that the formation of ether from alcohol is effected by substituting ethyle ($C_2 H_5$) for $\frac{1}{6}$ of the hydrogen of that body, the process of etherification by sulphuric acid was explained by a diagram, on which half the hydrogen in sulphuric acid was shown to change places with its analogue ethyle in alcohol ; and that

the peculiarity of the process, *i.e.* its continuity, is owing to this change of place between hydrogen and ethyle, first taking place in one direction and then in the opposite; that is, that sulphuric acid becomes sulphovinic acid by taking up ethyle instead of an atom of hydrogen, and that it is then re-converted into sulphuric acid by resuming hydrogen instead of this ethyle, the first change forming water, the second ether.

By using successively two different alcohols, it was shown that the two steps of this decomposition can be separated and their reality proved. The process of etherification is thus effected by a succession of double decompositions, each of which considered individually is perfectly conformable to the law of definite proportions; but the alternation and continuous succession so clearly proved in them, is a fact unexplained by that law. A complete analogy between this process and the more familiar cases of chemical action is therefore only to be established by finding in these latter a similar atomic motion.

A little reflection is sufficient to show that such a motion actually exists. The fact of diffusion is in reality nothing but a change of place between atoms, effected by the mere action of the particles on one another; and there are many mechanical evidences of the communication of momentum from masses to atoms, and inversely.

It seems perhaps difficult to reconcile the apparent rest of the constituents of a mass with the existence of a continuous atomic motion; but there are many cases in which a rapid and continuous motion produces to our senses the appearance of a phenomenon at rest: thus, the rapid revolution of a white sphere produces the appearance of a circle at rest when

seen in front, and that of an ellipse when viewed obliquely.

There are of course many points of view from which the motion of atoms may be considered ; but it is inasmuch as it produces or facilitates decomposition, that the chemist has to regard it. We have in etherification an evidence of the tendency of atoms of analogous nature to change places continuously ; and it is natural to suppose that the facility of this interchange must be greater in proportion to the analogy between the molecules, and greatest between like molecules. The lecturer expressed a confident hope that he would soon be able to give a direct experimental evidence of this conclusion, and proceeded to show how the admission of it explains, without the supposition of occult forces, the occurrence of double decompositions and the action of masses.

The exchange of analogous particles actually constitutes double decomposition ; and its occurrence in alternately opposite directions causes the two substances used to alternate with the two other compounds formed by the exchange of their bases ; so that in such a mixture, four substances are constantly to be found, the quantity of each substance corresponding to the average number of atoms which, in each moment of time, are in that state of combination.

Now it is clear that if an equal number of atoms of a hydrogen-salt, and of an iron-salt, reacting on one another, form a certain amount of the products of their double decomposition, a greater number of those products will be formed by doubling the quantity of the hydrogen-salt ; for, the facility of interchange of iron with hydrogen remaining the same, the atoms of the iron-salt will then come more frequently in contact with those of the hydrogen-compound. Thus,

on mixing a solution of sesquichloride of iron with sulphocyanide of hydrogen, a deep red colour gave evidence of the interchange of iron and hydrogen, forming sulphocyanide of iron and hydrochloric acid : but this exchange was not an operation effected once for all on the decomposing substances just coming in contact, but is constantly going on in the mixture ; and the quantity of the products of this interchange remains constant, because a similar double decomposition, equal in absolute number of atoms per unit of time, is constantly going on between these products, reproducing the original compounds. In evidence of this, the counterpart of the decomposition of sesquichloride of iron by hydrosulphocyanic acid was shown in the expulsion of this last acid by hydrochloric proved by the gradual diminution of the red colour on adding hydrochloric acid.

It is well known that caustic soda expels ammonia from its salts. But ammonia also expels soda : for it was shown, that a mixture of ammonia and hydrochlorate of soda dissolves less chloride of silver than the same quantity of ammonia alone ; and consequently, that a saturated solution of chloride of silver in aqueous ammonia is precipitated by dissolving chloride of sodium in it. The same occurs with the ammonio-sulphate of copper.

In conclusion, the lecturer referred to the question of the relative velocity of transfer of analogous atoms in opposite directions, which necessarily determines the proportion of the elements of two salts, contained in the form of their products of double decomposition, on these salts being mixed. On the mixture of equivalent proportions of a couple of salts in aqueous solution, a certain amount of decomposition ensues, forming two other salts, and the chemical force may

be considered proportional to the quantity of one couple compared to that of the other. Now as the proportion is only kept up by the number of exchanges in the one direction being ABSOLUTELY the same in each moment of time as those in the opposite direction, it is clear that the relative velocity of interchange must be greatest between the elements of that couple of which the quantity is least; and chemical force must be inversely proportional to the velocity of these interchanges.

ON ETHERIFICATION.*

THE question of the transformation of alcohol into ether and water by the agency of sulphuric acid, may be divided into two parts; first, the relative weight of the substances engaged in the reaction; and, secondly, the actual process by which the transformation is effected. In a preceding memoir, read before the British Association last autumn, I briefly described the formation and properties of certain new ethers, which seemed to solve at least the first part of this question, *i. e.* the relative formulæ of alcohol and ether. I now lay before the Society a more exact account of the process by which these bodies were obtained, with their analysis, to which I have to add a direct evidence of the process by which sulphuric

* [From *The Quarterly Journal* of the Chemical Society of London, vol. iv. (1852), pp. 229-239.]

acid effects the decomposition of alcohol ; and, finally, I will describe a reaction with the acids of the adipic series, in which the formation of a peculiar series of bodies gives evidence that the formulæ of these acids should be halved similarly to those of the alcohols. But first, a few words on the previous views of the subject, as I understand them.

Of the relative formulæ of alcohol and ether, there have been especially two views ; one of which represented ether as the compound of olefiant gas with one atom of water, and alcohol as the compound of this same hydrocarbon with twice as much water ; the other considered ether as the oxide of a peculiar hydrocarbon C_4H_{10} , and alcohol as the oxide of another hydrocarbon C_2H_6 . The first of these views was derived from a consideration of the analogy of the ethers with the salts of ammonia ; the second was formed rather from a comparison with metallic salts. To the French school, with Dumas at its head, we owe the former, and the great Berzelius suggested and advocated the latter. The study of the transformations of alcohol, and especially that by sulphuric acid, led to the modification of these views, and to the formation of others containing certain points of each ; and the most important of these is certainly the theory of Liebig, who, giving the name of ethyl to the hydrocarbon C_4H_{10} , represented ether as its oxide, and alcohol as the hydrate of that oxide. From novel and highly important considerations, Gerhardt arrived at the formulæ of Berzelius, and compared alcohol in its reactions to an acid. The process of etherification, of which the continuous nature had been discovered by Boullay, was, from the different points of view afforded by the above-mentioned formulæ, of course represented

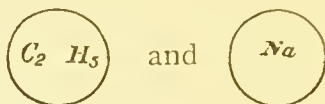
differently. Berzelius and the contact-school, seeing in ether a more complex atom than alcohol, and considering the apparently indefinite action of sulphuric acid, were especially struck with the difference between etherification and other cases of chemical action, and supposed some different force must be active in it, which was christened *catalysis*. It was certainly an important step towards the philosophical solution of the question, which Liebig made, in urging the resemblance to chemical action, and explaining more successfully than Hennel had been able to do, the process by chemical affinity, overcome successively by the decomposition of sulphovinic acid by heat. The mutual action of these various theories had exercised a decomposing influence upon them all, and the elegant experiments by which Graham shewed the untenable nature of the chemical theory, afford conclusive evidence of that decomposition. Now I submit that the theory here laid before you, with its experimental conclusions, combines the requisitions of the several parties in this great discussion, and may be considered as closing it amicably, by shewing that each point of view contained part, and an important part, of the facts. The explanation of the process is composed of two parts—first, proving in etherification the occurrence of decompositions strictly analogous to common phenomena usually attributed to chemical affinity, and as explicable by such a name as those phenomena may be; and, secondly, on finding that over and above the commonly observed phenomena of chemical action, there occurs in this process a new circumstance, it will be necessary to prove the occurrence of this circumstance in the more familiar cases.

Formation of ether by double decomposition.—In the

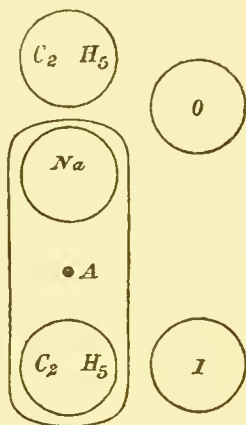
paper above referred to, I stated the fact of this reaction, which consists in the elimination by metallic sodium of the hydrogen in alcohol, which has to be replaced by ethyle, and the action of the iodide of ethyle on the compound thus formed, which, from its analogy with the hydrate of potash, I will call *ethylate of potash*.* It is important that the alcohol used in this and all similar reactions be as anhydrous as possible ; and the naphtha which surrounds the sodium must be removed completely by drying with bibulous paper and immersion for a few seconds in a small portion of absolute alcohol, which serves successively to rinse all the pieces of metal used in one experiment. The pieces of sodium thus purified are thrown, one at a time, into the alcohol which is to be transformed into ether, until the liquid is completely saturated with them ; after cooling, it is treated with iodide of ethyle, and distilled, the ether passing over with alcohol vapour and some of the iodide. To remove these admixtures, the distillate should be treated with sodium, which, as long as alcohol is present in equivalent quantity with the iodide, forms more ether, and when all the iodide has been thus decomposed, forms with the remaining alcohol, ethylate of sodium, from which the ether may be distilled off in a state of perfect purity. Prepared in this manner, ether is identical in its boiling-point and all its properties with that prepared by the action of sulphuric acid.

* The atomic weight of hydrogen and the metals, iodine, &c., is in this paper according to Laurent and Gerhardt's notation, assumed at half their equivalents. The compound radicals methyle (CH_3), ethyle (C_2H_6), amyle (C_5H_{11}) are of course reduced to the same unit.

The reaction is easily understood by the following diagram, in which the atoms



are supposed to be capable of changing places by turning round upon the central point A.



It is clear that we thus get $\text{C}_2\text{H}_5\text{O}$ and NaI . The circles are merely used to separate off the atoms or units of comparison. To express the corresponding decomposition of iodide of ethyle by hydrate of potash, forming alcohol, we should replace the ethyle of the sodium-compound by hydrogen, and the same change of place between sodium and ethyle forms $\text{C}_2\text{H}_5\text{O}$ (alcohol) and NaI .

Three-carbon ether, Ethylate of methyle, or Methylate of ethyle.—This compound may be prepared by the action of iodide of ethyle on the methylate of sodium, CH_3O , or inversely, by acting on ethylate of sodium

by iodide of methyle. Of these two processes, I however prefer the former, from the fact of iodide of ethyle boiling at so much higher a temperature than the ether, that any excess of it is easily separated by distillation. This ether is purified in the same manner as the preceding one. On account of its more powerful action, I generally preferred potassium to sodium for the removal of the last traces of alcohol from an ether; and in order that the action of the metal might be complete, the distilling apparatus was so arranged that the distillate constantly flowed down into the retort until the action had completely ceased, and then only was the ether distilled over from the fixed products of that action. The boiling-point of this ether is 11° C., and it was therefore usually distilled simply by removing from the retort the frigorific mixture by which it was retained in the liquid state. In order to effect its combustion, a small quantity was introduced into a strong bulb at the extremity of a piece of thermometer tubing, about 6 inches long, which had been previously weighed, and which being bent at a right angle, could be fixed by means of a cork into the end of a combustion-tube, open at both ends, and was in the power of the operator.

By this process, the ether being burnt by oxide of copper, the following results were obtained :

0.2215 grm. of liquid gave :
 0.482 „ „ carbonic acid, and
 0.2685 „ „ water.

The percentage composition as deduced from this, is :

	By Experiment.	By Calculation.	Difference.
Carbon . . .	59.39	60.00	0.61 -
Hydrogen . .	13.46	13.33	0.13 +
Oxygen . . .	27.15	26.67	0.48 +

The density of its vapour was found to be :

By Experiment.	By Calculation.	Difference.
2.158	2.084	.074

Weight of globe and air at 12° C. and 30.05 in. bar. = 53.6240 grms.

Weight of globe and vapour, the temp.

at moment of sealing the point 23°.5

C., and bar. 30.05. = 54.1790 „

Capacity of globe = 438 cub. centi.

Residual air at 16° C. and 30.05 bar. . = 23 „

Hence its formula is $\begin{smallmatrix} \text{C}_2 & \text{H}_5 \\ \text{C} & \text{H}_3 \end{smallmatrix} \text{O}$, or empirically $\text{C}_3 \text{H}_8 \text{O}$.

Now it being thus established beyond doubt that this substance contains 1 volume ethyle, 1 vol. methyle, with 1 vol. oxygen, the three condensed into two volumes, and the two opposite modes of preparing it proving that the two atoms of hydrocarbon are contained in *like* manner in it, we may view it either as the ethylate of methyle, *i. e.* alcohol in which one atom of hydrogen is replaced by methyle, or else as methylate of ethyle. I am, however, convinced that the simplest view that can be formed of its constitution is to be gathered from a comparison with water, from which it may be produced by replacing one atom of hydrogen by ethyle and the other by methyle.

Seven-carbon ether, Amylate of ethyle, or Ethylate of amyle.—This ether is one of the most easily prepared of these peculiar bodies, and is perfectly identical when prepared from amylic alcohol and iodide of ethyle, or ethylic alcohol and iodide of amyle. I have prepared it in considerable quantity by each process, and could discover in no respect any difference of properties between the products ; its boiling-point

is 112° C. Combustion performed with oxide of copper.

0.2350 grm. yielded :

0.624 „ of carbonic acid, and

0.276 „ of water ;

or in 100 parts.

	Experiment.	Calculation.	Difference.
Carbon . . .	72.42	72.41	0.01 +
Hydrogen . .	13.99	13.79	0.20 +
Oxygen . . .	13.59	13.80	0.21 -

Its formula is therefore $\text{C}_2\text{H}_5\text{O}$, or empirically $\text{C}_7\text{H}_{16}\text{O}$.

The density of its vapour was found to be :

By Experiment.	Calculation.	Difference.
4.042	4.031	0.011

Weight of globe and air at 11° C., bar.

at 29.60 in. = 93.7790 grms.

Weight of globe and vapour, the temp.

at moment of sealing being 135.5°

C., and bar. 29.64 = 94.6755 „

Capacity of globe = 377 cub. centi.

Residual air at 25° C., and 29.60 bar. . = 3 „

Increased expansion of glass globe at

135° C. = 0.92 „

Six-carbon ether.—Boils at 92° C.; analysis as follows:

0.2050 grm. of liquid gave as the produce of combustion :

0.528 „ „ carbonic acid, and

0.256 „ „ water ;

which gives in 100 parts :

	Experiment.	Calculation.	Difference.
Carbon . . .	70.244	70.588	0.344 -
Hydrogen . .	13.873	13.725	0.148 +
Oxygen . . .	15.883	15.686	0.197 +

Hence the formula $\text{C}_6\text{H}_{14}\text{O}$.

The density of its vapour was found to be :

By Calculation.	By Experiment.
3.546	3.75
Weight of globe and air, temp. 10° C., bar. 29.72 in. = 90.689 grms.	
Weight of globe and vapour temp. at moment of sealing the point 110° C., and bar. 29.72 in. = 91.553 „	
Capacity of globe = 407 cub. cen.	
Residual air at $19\frac{1}{2}^{\circ}$ C., and 29.93 inches bar. = 10.75 „	

A second experiment gave nearly analogous results :

Weight of globe and air, temp. 11.5° C., bar. 30 in. = 85.0855 grms.	
Weight of globe and vapour, temp. at moment of sealing, 111.5° C., bar. 30 in. = 85.8925 „	
Capacity of globe = 377 cub. centi.	
Residual air at 22° C., and 30 in. bar. = 4.5 „	

Calculated density from this latter experiment = 3.73.

In my former paper, I showed how the formation of these intermediate ethers proves the atomic weight of the alcohols to be half that which they have of late years been considered, so that their equivalent occupies in the state of vapour the same volume as that of ether, water, &c. It is of course only a *relation* which I here establish, and if any chemists prefer doubling the present formulæ of ether, water, and all the metallic oxides, they will accomplish the same object in an unnecessarily clumsy manner. But the same arguments which require me to halve the atomic weight of alcohol must of course apply to its compounds, and sulphovinic acid, which is nothing else

than the sulphate of alcohol, as represented by the formula $\frac{A}{H}SO_4$; and the process of etherification is at once explained; for by the reaction of this sulphovinic acid upon alcohol, we have at once ether and sulphuric acid, which again reacts upon the atoms of alcohol, forming with the first, $\frac{A}{H}SO_4$ and $\frac{H}{H}O$, and with the second $\frac{A}{A}O$ and $\frac{H}{H}SO_4$. Thus it is that the sulphovinic acid formed at the end of a long process of etherification is not the same as that which formed at first, but being perfectly like, it cannot of course be distinguished from it. To prove this point, I made sulphuric acid react successively upon two alcohols, so that it took the hydrocarbon from the first, and gave it up to the second, forming an intermediate ether, and finding only the second alcohol to react upon, remained at last combined with its hydrocarbon alone. The experiment was performed in the following manner: Sulphamylic acid was prepared by the action of sulphuric acid upon its equivalent weight of fusel oil, and this compound was treated with vinic alcohol by the continuous process, until the distillate consisted of pure 4-carbon ether. The residue was then examined, and found to contain *no* sulphamylic acid, but only sulphovinic, the 7-carbon ether being easily separated out from the first portions of the volatile product. I next tried the action of sulphuric acid upon a mixture of equivalent weights of the two alcohols, expecting similarly to have the production of the 7-carbon ether, and the result fully justified my expectations; for on treating the mixture by the continuous process, a distillate was obtained consisting of two liquids, water and a light ethereal

liquid, which, after two distillations over fused potash, was distilled with the thermometer, and rose from 40° to 180° . A considerable portion was separated by repeated distillation at the temperature of 112° C. It shewed by combustion the exact composition of the 7-carbon ether.

0.25075 grm. of ether yielded :
 0.6665 „ „ carbonic acid, and
 0.3100 „ „ water ;

which gives the following percentage :

	Experiment.	Calculation.	Difference.
Carbon . . .	72.46	72.41	0.05 +
Hydrogen . .	13.73	13.79	0.06 -
Oxygen . . .	13.81	13.80	0.01 +

The last portions of the distillates were added together and re-distilled, their temperature rising rapidly to 176° , where it remained stationary for some time, and the liquid which came over at this temperature shewed the composition of amylic ether. Thus :

0.2045 grm. of distillate produced :
 0.5685 „ „ carbonic acid, and
 0.2595 „ „ water,

giving the following percentage composition :

	Experiment.	Calculation.	Difference.
Carbon . . .	75.81	75.95	0.14 -
Hydrogen . .	14.09	13.92	0.17 +
Oxygen . . .	10.10	10.13	0.03 -

The smell of common ether was very perceptible in the first portions of the mixture which came over. It is thus clear that by the action of sulphuric acid on the mixed alcohols, three ethers are formed by the reaction of sulphovinic and sulphamylic acids on each

of the alcohols respectively. On treating in a similar manner a mixture of equivalent parts of methylic and amylic alcohols, a corresponding result was obtained, the products being, however, more easily separated than in the preceding instance, owing to the greater difference of their boiling-points. The experiment was performed in the following manner: 17 oz. of aqueous methylic alcohol was mixed with 38 oz. of fusel oil, which had been ascertained by a previous trial to contain the equivalent quantity of amylic alcohol; 7 oz. of this mixture were added to 5 oz. of sulphuric acid, and heated to 120° , at which temperature the etherification commenced; the mixed alcohols were allowed to run into the retort, so as to maintain the level of the liquid in it a little higher than it had been at first, and in this manner the whole of the mixture was converted into a colourless distillate, composed of about one volume of water to three of the mixed ethers, and possessing a faint smell of sulphurous acid. The theory of the purification of this mixture by distillation over dry hydrate of potash, is easily intelligible from the fact that that substance becomes transformed in contact with alcohol into ethylate of potash, with formation of water; and similarly into amylate of potash by the action of amylic alcohol. Thus it is that the whole of these alcohols are kept back by the potash, and the excess of it even takes up pretty completely the water, so that the mixture of ethers, after this treatment, is scarcely acted on at all by potassium. We have in these reactions the best evidence of the nature of the action of sulphuric acid in forming common ether, or in accelerating the formation of the so-called compound ethers; for acetic ether is formed from acetic acid, just as ethylic ether from alcohol, by the replace-

ment of hydrogen by ethyle. And if the circumstance of containing hydrogen, which is replaceable by other metals or radicals, be the definition of an acid, we must consider alcohol as acting the part of an acid in these reactions. Common ether is its ethyle-salt, the 3-carbon ether is its methyle-salt, and so on, just as the potassium-alcohol or ethylate of potash is its potassium-salt.

But before proceeding further in the investigation of these circumstances, I must beg leave to direct your attention for a moment to the relation between alcohol and acetic acid, and show how the conclusions just arrived at concerning the former will be applicable to the atomic weight of the latter. You are aware that this acid is essentially monobasic in its characters, like the other terms of the series to which it belongs, and that, in conjunction with other reasons, this circumstance has been urged by M. Gerhardt as a ground for halving its formula. Now as acetic acid is formed from alcohol by replacing one-third of its hydrogen by oxygen, there are strong grounds for assuming a similar atomic constitution in both, and of writing acetic acid at half its usual atomic weight, in accordance with the reduced formula of alcohol. Viewing, therefore, alcohol as water in which half the hydrogen is replaced by ethyle, $\text{C}_2\frac{\text{H}_5}{\text{H}}\text{O}$, we shall consider acetic acid as containing one equivalent of oxygen in the place of two atoms of hydrogen of that radical, or $\text{C}_2\frac{\text{H}_3}{\text{H}}\text{O}$. Organic chemistry is replete with instances of differences similar to those between alcohol and acetic acid, and produced by the substitution of an electro-negative element for hydrogen; take for example phenylic alcohol, a feeble acid, in which the substitution of hyponitric acid for hydrogen

produces stronger and stronger acids up to carbazotic, a very strong acid ; or again, consider the diminution of the alkaline properties of aniline by the substitution of more and more chlorine for its hydrogen, until they entirely disappear in the trichloraniline, as shewn by Dr. Hofmann. Now we actually prepare acetic acid by the action of oxygen upon alcohol under certain circumstances, and observe a double decomposition perfectly analogous to that produced by chlorine in its action on hydrocarbons, water being formed, and the hydrogen thus taken out being replaced by oxygen ; but it is clearly not the basic atom of hydrogen in alcohol which is thus replaced, for acetic acid retains it with its characteristic properties heightened. It is, therefore, the hydrogen of the radical which is thus replaced by oxygen, and acetic acid differs from alcohol by containing, instead of ethyle, this other radical, differing from it by having oxygen in lieu of an equivalent of hydrogen, and which may be called *oxygen-ethyle*, or *othyle*. We are thus led to consider the atom of ethyle as containing half the number of atoms which are generally ascribed to it, and as occupying in the state of vapour two volumes and not four. But I endeavoured to obtain an experimental evidence of the correctness of this conclusion, and sought it in the decomposition of the acetates by heat, by which their elements separate into acetone and carbonate. In this decomposition, the process differs according to the two views of the constitution of acetic acid ; if the atom of acetate of potash be $\text{C}_4\text{H}_6\text{O}_4$, acetone and carbonate are formed by the division of one atom ; whereas, if the formula of the acetate be $\text{C}_2\text{H}_3\text{O}_2$, the reaction

consists in a double decomposition, by which CH_3 in one atom is replaced by KO , *i. e.* methyl by peroxide of potassium, or $\text{C}_2\text{H}_3\text{O}$ replaced by CKO_2 . To ascertain which of these two opposite views is the more correct, I dissolved in water equivalent weights of acetate of soda and valerate of potash, and evaporated rapidly to dryness. The mixed salts were introduced into a retort, and subjected to dry distillation, the oily distillate shaken with aqueous potash, to remove the acids which might have come over undecomposed, and after separation from the potash, distilled with the thermometer. By uniting the products of repeated distillations, a liquid was obtained, boiling with perfect regularity at 120°C ., and constituting nearly two-thirds of the original distillate. This body was found to possess the composition $\text{C}_6\text{H}_{12}\text{O}$, as shewn by the following combustion with oxide of copper.

0.704 grm. of carbonic acid and 0.2935 grm. of water were the results of the decomposition of 0.2690 grm. of the liquid; the percentage relations, as obtained by experiment and calculation, are as follows:

	Experiment.	Calculation.	Difference.
Carbon . . .	71.38	72.00	0.62 -
Hydrogen . .	12.12	12.00	0.12 +
Oxygen . . .	16.50	16.00	0.50 +

Hence the formula is, $\text{C}_6\text{H}_{12}\text{O}$, or empirically $\text{C}_4\text{H}_8\text{O}$.

The same experiment was performed with various other terms of the series, and similar results obtained, the details of which I will communicate on a future occasion. On distilling equivalent parts of an acetate and formiate, the corresponding reaction would con-

sist in the formation of a body having the composition of aldehyde, which is the hydruret of ethyle, as acetone is its methyle-compound.

The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of.

ON THE CONSTITUTION OF SALTS.*

CHEMISTS have of late years considerably extended the meaning of the term salt; acids and bases are now rather viewed as acid salts and basic salts respectively, than as compounds of fundamentally different arrangement, and there seems reason to believe that the molecular structure of the so-called simple bodies is analogous to that of salts. Thus any view which best explains the properties of salts may be expected to apply ultimately to the molecular structure of matter in general.

It was remarked that a serious error had crept into chemical science by the introduction of a different unit of comparison in organic chemistry to that which is employed in the inorganic department of the science.

* [From *Report of the Twenty-first Meeting of the British Association for the Advancement of Science*, 1851, part 2, p. 54.]

The removal of this error and adoption of an uniform standard of comparison, naturally leads to viewing chemical action as consisting in substitutions rather than in direct combinations. The best studied processes of organic chemistry have been found to consist of double decompositions. Numerous other instances were mentioned, in which the result may be far more simply explained by a process of double decomposition than by the supposition of unknown predisposing affinities invented for each ; and various arguments were adduced why the same mode of reasoning ought to be extended even to the simplest phænomena of inorganic action generally considered as mere combinations or separations. It was shown that water may be assumed as a very general if not universal type and standard of comparison, by viewing other bodies as formed from it by the replacement of one or more atoms of hydrogen in water by their equivalent of various simple or compound radicals. The atom of radical thus replacing hydrogen is sometimes equivalent to one atom of that element ; in other cases it is equivalent to two. The difference between monobasic acids, such as nitric and bibasic acids as sulphuric, were shown to follow as a necessary consequence of such a difference of the respective radicals NO_2 and SO_2 .

ON THE CONSTITUTION OF SALTS.*

THERE is strong reason for believing that all questions concerning the chemical constitution of matter will be most tangible when considered from the point of view of the constitution of salts, which are the groups whose arrangement and transformations are most susceptible of being ascertained experimentally. The elementary bodies themselves have been now shown † to obey a certain force of combination between their particles, analogous though generally inferior to that which holds together the constituents of a salt; and any general conclusions which may be established for salts, will therefore extend to them. Now, to have clear and connected notions of any order of phænomena, it is necessary to be able to judge of the various cases belonging to it from the same point of view; or, in other words, to have a uniform standard of comparison. Thus if the value of mechanical forces had to be compared, it would evidently not do to measure the one in pounds and the other in kilogrammes, unless the relative value of these units were known, *i. e.* unless the statement made in the one could be reduced to its equivalent in the other. Such unity has as yet been but little attended to by the majority of chemists; and the different branches of the science remaining disconnected, their efforts were directed to establish details rather than general laws. Thanks to the numerous

* [From *The Chemical Gazette*, vol. ix. (1851), pp. 334-339.]

† See Mr Brodie's research "On the Condition of certain Elements at the moment of Chemical Change."

facts which have been thus established, it is now possible, and even necessary, to do something more. The researches of MM. Laurent and Gerhardt have been mainly directed to this point, and it is well known how fruitful their conclusions have already proved. The following remarks have an intimate connexion with those conclusions, and will hardly be intelligible without a knowledge of them.

We are all agreed that chemistry is concerned with the material process of the transformations and changes which matter undergoes, and that the study of the properties of matter in themselves, as long as they undergo no change, belongs to physics. The chemical formulæ, by which we describe more briefly than by words the transformations supposed or known to take place, have as yet answered that purpose very imperfectly, and have presented great irregularity of method ; for although generally denoting a certain arrangement of atoms, or at least certain differences of arrangement, they are sometimes used to describe the origin of a compound or its decompositions, without forming any other representation of its actual constitution than what may be contained in such a statement. M. Gerhardt has, in a recent memoir published conjointly with M. Chancel, given considerable development to this latter method ; and his so-called synoptic formulæ will, I think, be found very suggestive and useful expressions. But formulæ may be used in an entirely different, and yet perfectly definite manner, and the use of two distinct points of view will perhaps not be unserviceable. They may be used as an actual image of what we rationally suppose to be the arrangement of constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary

system ; and decompositions may be actually effected between them by the exchange of a molecule in one group for a molecule in another. Gerhardt's formula for sulphate of soda (if he extends his principles to inorganic chemistry) would be sulphuric acid plus soda minus water. This, no doubt, gives a possible origin of the salt, but by no means a possible decomposition ; in other instances the inverse would be the case. But the term sulphate of soda does not mean a body formed in any one particular way ; it is equally applicable to the product of the action of sulphuric acid on chloride of sodium, or on carbonate of soda, or even to the product of the action of soda on sulphate of iron. The written name should be made to represent what we conceive a compound *to be*, and should be such that it might be formed by any one of the various processes by which the compound may be prepared. Sulphate of soda is a physical term, and corresponds to purely physical properties ; for the substance subscribed by it does not by itself undergo any change, but only when acted upon by certain foreign substances under suitable circumstances.

When we study a molecule by itself, we study it physically ; chemistry considers the *change* effected by its reaction upon another molecule, and has to describe the process by which that change is effected. A chemical decomposition should therefore be represented by the juxtaposition of the formulæ of the reacting substances, and by effecting in these formulæ the change which takes place in the mixture.

The adoption of such a method will of course necessitate the adoption of types, from which, by the replacement of certain elements or molecules, we can deduce the constitution of more and more complex groups. I believe that throughout inorganic chemistry,

and for the best-known organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen, thus $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{O}$. In many cases a multiple of this formula must be used, and we shall presently see how we thereby get an explanation of the difference between monobasic and bibasic acids, &c.

I will here give a few examples of the application of this universal type to the formulæ of common substances. The experiments of M. Chancel, agreeing in result with my own, have clearly proved that the numerous family designated as hydrated oxides are not formed by the juxtaposition of an atom of water with an atom of metallic oxide, *e. g.* $\text{K}_2\text{O} + \text{H}_2\text{O}$, but that the equivalent of the molecule is half of that quantity, namely $\begin{smallmatrix} \text{H} \\ \text{K} \end{smallmatrix} \text{O}$; they are not compounds of water, but products of substitution in water. This fact is as applicable to the compound as to the simple radicals; and alcohols, which are truly hydrated oxides, must be considered as products of substitution of the compound radicals, methyle, CH_3 ; æthyle, C_2H_5 ; amyle, C_5H_{11} ; œnanthyle, C_7H_{15} (Buis), &c., for half the hydrogen of water, $\begin{smallmatrix} \text{H} \\ (\text{CH}_3) \end{smallmatrix} \text{O}$, $\begin{smallmatrix} \text{H} \\ \text{C}_2\text{H}_5 \end{smallmatrix} \text{O}$, &c. The anhydrous oxides of metals have both atoms of hydrogen replaced by the metal, as $\begin{smallmatrix} \text{K} \\ \text{K} \end{smallmatrix} \text{O}$, in the same way as common æther and its homologues have æthyle in place of both the atoms of hydrogen.

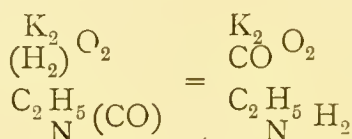
In extending this mode of notation to salts and compound æthers, we must of course keep carefully in view the capacity of saturation of their acids, writing the monobasic acids as hydrochloric,

nitric, acetic, &c., at half their usual equivalents, ClH , NO_3H , $\text{C}_2\text{H}_4\text{O}_2$, but retaining the customary atomic weights of the bibasic acids, as sulphuric, carbonic, oxalic, &c.

As alcohol is truly an acid in its reaction, we must of course consider the potassium-alcohol, $\text{C}_2\text{H}_5\text{O}_\text{K}$, as its salt, though alkaline in its reactions. We only need to replace 2 atoms of hydrogen in the radical of this salt by oxygen, to have a compound of which the saline character is acknowledged, acetate of potash, $(\text{C}_2\text{H}_3\text{O})_\text{K}\text{O}$. The most simple manner of representing the rational constitution of this compound is to state that it contains, in lieu of the æthyle of the former salt, an oxygen-æthyle, $\text{C}_2\text{H}_3\text{O}$, which we may term othyle. If the 2 atoms of hydrogen in water were replaced by this othyle, we should have anhydrous acetic acid, $(\text{C}_2\text{H}_3\text{O})_\text{O}$. In fact, the so-called anhydrous acids are nothing else than the *æthers* of the hydrated acids.

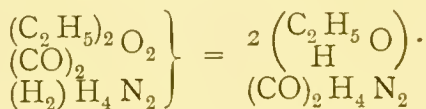
Again, by replacing the potassium in the æthylate, $\text{C}_2\text{H}_5\text{O}_\text{K}$, by its equivalent of cyanogen (which may be effected by the action of iodide of cyanogen), we obtain a compound of the composition $(\text{NC})\text{C}_2\text{H}_5\text{O}$, that is, cyanic æther. It is well known, from Wurtz's elegant researches, that by acting upon this body by hydrate of potash, we obtain carbonate of potash and æthylamine; that is, in the place of carbonic oxide in the cyanate, we get hydrogen, and reciprocally with the hydrate. Now can this exchange be represented more simply than by stating the fact, that,

in the following diagram, the hydrogen of the 2 atoms of hydrate of potash changes places with the carbonic oxide of the cyanate :—



1 atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, holds together the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\frac{(\text{CO})}{\text{K}_2} \text{O}_2$.

If we knew how to form the compound COCl , *i. e.* phosgen, with half as much chlorine, it would be easy, by the reaction of it upon our æthylate of potassium, to prepare oxalic æther (and chloride of potassium). Oxalic æther is therefore alcohol in which the basic hydrogen is replaced by carbonic oxide with twice the equivalent that it possesses in the carbonates; and the best evidence of the truth of this view is afforded by M. Dumas's elegant reaction of ammonia upon the æther, forming the compound of amidogen with carbonic oxide (oxamide), and replacing the carbonic oxide by hydrogen, *reproducing alcohol* :—



Sulphurous acid is another radical capable of replacing hydrogen; and the sulphates are thus reduced to our type, being bibasic for the same reason as the carbonates. We have thus for sulphuric acid, $\frac{\text{SO}_2}{\text{H}_2} \text{O}_2$;

acid sulphate of potash, $\text{SO}_2 \text{O}_2$; neutral sulphate, $\text{K}_2 \text{SO}_4$, &c.

There are various reactions, both of formation and decomposition, of sulphates, which bear out this view; for instance, chlorosulphuric acid, $\text{SO}_2 \text{Cl}_2$, in contact with 2 atoms of water, at once replaces half the hydrogen in both by SO_2 , forming 2 (ClH) and $\text{H}_2 \text{SO}_4$. And again, the difference of the action of zinc upon sulphuric acid according to the concentration, evolving at one time hydrogen, at another sulphurous acid, affords evidence that the sulphurous acid is contained in a manner similar to the hydrogen.

Nitric acid presents, according to the usual view of its constitution, a singular difference between its behaviour to organic and to inorganic compounds; but this difference is owing merely to the error of that view. We are taught that nitric acid combines directly with mineral bases; but when reacting upon hydrogen compounds, it has a powerful tendency to replace hydrogen by hyponitric acid. Now if hydrogen, in organic compounds without number, be replaceable by hyponitric acid, why should not also the hydrogen in hydrate of potash be so replaceable? The product of that substitution would be no very improbable body, only common nitrate of potash, $\text{K}(\text{NO}_2) \text{O}$.

One more example, and I have done. Chlorine is well known to react upon hydrogen-compounds by replacing hydrogen by chlorine, with formation of hydrochloric acid. So it is also when it reacts upon water in presence of bases, $\text{H} \text{Cl}$ (hydrated hypo-

chlorous acid), and ClH being formed. In like manner we have, for the series of oxygen acids of this radical, the formulæ $\begin{smallmatrix} (\text{ClO}) \\ \text{H} \end{smallmatrix} \text{O}$, chlorous acid ; $\begin{smallmatrix} (\text{ClO}_2) \\ \text{H} \end{smallmatrix} \text{O}$, chloric acid ; $\begin{smallmatrix} (\text{ClO}_3) \\ \text{H} \end{smallmatrix} \text{O}$, perchloric acid.

In order to accomplish what I above alluded to as a desideratum for the explanation of chemical reactions, namely effecting between the formulæ of the reagents the interchange supposed to take place in the mixture, I have fixed the symbols of those atoms which have to change places upon the extremities of a piece of card, so fixed by a pivot to the board that by turning round 180° it reverses the positions of the exchanging atoms.

I would not have brought before the public considerations so purely theoretical as the above, had I not found the conclusions of considerable practical utility in the study of reactions.

In the theory of types, we owe to M. Dumas an idea which has already been the vehicle of many an important discovery in science, and which is undoubtedly destined to receive still more general application.

To prevent misunderstandings, it may be as well to state, that the radicals which I have here so freely used are not supposed to be in their compounds absolutely the same as in the free state. The same remark applies with equal force to metallic bodies, which on entering into combination give off a certain amount of heat, and thus assume different properties. To say that metallic zinc is contained in its sulphate is an expression authorized by usage, but is only strictly true by abstraction from most of the properties of the metal. The material atom, which under certain

circumstances possesses the properties which we describe by the word "zinc," is no doubt contained in the sulphate, but with different properties, and in the chloride with properties different from either; so also of the compound radicals.

It is to be hoped that we may soon be able to give an account of the nature of the processes by which these changes of properties are effected; but that task can only be entered upon when we have obtained exact determinations of the relative momentum of atoms in various compounds, the proportion of which to their masses determines their physical and chemical properties.

ON GERHARDT'S DISCOVERY OF ANHYDROUS ORGANIC ACIDS.*

THE discovery by M. Gerhardt of a number of anhydrous organic acids has thrown so much light on one of the most important questions of chemical philosophy, that it constitutes one of the most remarkable illustrations of the manner in which the rich materials of organic chemistry may be brought to bear on the explanation of the phenomena of chemical action and the laws of chemical combination.

It is not unworthy of remark, that the bodies pre-

* [From *Notices of the Proceedings at the Meetings of the Members of the Royal Institution*, vol. i., 1851-1854, pp. 239-242.]

pared by Gerhardt had for some years past been supposed to exist ready formed in combination with water and other bases, and that the chief objection to that supposition was founded on the circumstance of their never having been separated from such combination, and presented in an isolated form. In fact Gerhardt has supplied the very link in the chain, which was expected to constitute evidence for a familiar theory of the constitution of salts. But the process by which the result was attained is even more important than the result itself, and has led to our drawing from that result a conclusion different from that which was generally expected. Chemistry aims at discovering the nature of that action by which substances of opposite properties undergo those remarkable changes which we call chemical combination; and it naturally follows from this view of its objects, that chemical science is more advanced by the discovery of a new *process* than by the discovery of a new *substance*; and its theories are more immediately affected by the nature of a process of change than by any physical fact, such as the existence of a peculiar body or class of bodies. Thus it is that the method of isolating the anhydrous organic acids, has afforded evidence of a new view of the constitution of acids and salts.

A few words may serve to give an idea of the previous state of the question.

Compounds of oxygen-acids were supposed to consist of the anhydrous acid united with an oxide. Thus hydrated sulphuric acid was represented as containing the anhydrous group SO_3 plus an atom of water H_2O ; and in the saturation of this hydrated acid by a base such as potash, it was conceived that this oxide replaced the water. The existence of an-

hydrous sulphuric acid in an isolated state, and the fact that it so readily combines with water, was urged as an argument in favour of this theory; and the same holds good with phosphoric, carbonic, sulphurous, lactic, nitrous, and even (according to the recent discovery of Dessaignes) nitric acid.

However simple this view might appear and however satisfactory it might be in explaining those cases of combination for which it was specially intended, chemists soon became acquainted with bodies perfectly analogous in their general properties to the oxygen-acids, and producing by their action upon bases similar effects, but which, from the fact of their containing no oxygen, could not possibly be conceived as made up of water and an anhydrous-acid. For instance, hydrochloric acid was proved, both analytically and synthetically, to be composed of nothing but chlorine and hydrogen; and when it combines with potash, the hydrogen is found to leave the chlorine, whilst potassium takes its place.

Being desirous of simplifying as far as possible their views of these phenomena, and of extending the same explanation to all like cases, certain chemists were led to imagine a new mode of representing the constitution and reactions of oxygen-acids, which had the advantage of connecting the two classes of analogous reactions by the same theory. This consisted in conceiving, that in the formation of a hydrated acid, a compound radical is produced in combination with hydrogen; so that hydrated sulphuric acid is the hydrogen-compound of SO_4 , in the same way as hydrochloric acid is the hydrogen-compound of chlorine. There were many arguments in favour of this view, amongst which the most prominent was derived from the fact, that when a salt of the one class, as

chloride of potassium, decomposes a salt of the other, as sulphate of silver, the result is exactly in conformity with what must occur on the supposition of the compound radical; and in like manner, the electrolytic decomposition of a sulphate moves the group SO_4 to the positive pole, where it either combines with a metal or undergoes decomposition.

One of the strongest arguments against the view that the oxygen-acids contain water, is afforded by the results of recent researches (especially of MM. Laurent and Gerhardt) on the atomic weight of acids. Those chemists have rendered more definite and exact than they had been before, our ideas on the distinctions between monobasic, bibasic, and tribasic acids, and have clearly established that the correct expression of the atom of nitric acid must be such as contains half as much hydrogen as is contained in one atom of water (inasmuch as water is bibasic, and nitric acid monobasic). Of course this proportion may be as well established by doubling the atomic weight of water as by halving that of hydrated nitric acid; but either way it is clear that hydrated nitric acid cannot *contain* water.

Such was the position of the question, when an English chemist proved that the formation of ether from alcohol (which was considered chemically as the hydrate of ether), does not consist in a separation of two already formed compounds, but in a substitution of hydrogen by the organic radical ethyl. A similar fact M. Gerhardt has proved respecting a great number of organic acids, by preparing bodies which stand to them in the same relation as ether does to alcohol.

The researches of M. Cahours had led to the discovery of a series of bodies necessary for Gerhardt's process. These were obtained by the action of penta-

chloride of phosphorus on various hydrated organic acids, and consisted of chlorine combined with the oxygenized radical of the acid. Thus from benzoic acid was prepared the chloride of benzoil, C_7H_5OCl , and the corresponding bodies from cuminic, cinnamic, and various other acids. Gerhardt has since made by the same process the body C_2H_3OCl , which is the chloride of the radical of acetic acid, called *othyl*. Now, on bringing any one of these chlorides in contact with the potassium-salt of the corresponding acid, the chemical force of combination between chlorine and potassium induced the decomposition.

These results can be most simply stated in the form adopted by M. Gerhardt the discoverer, which consists in comparing the composition of these bodies with that of water, from which they are formed by the substitution of one or both atoms of hydrogen by organic radicals.

Thus water being represented by the formula $\begin{smallmatrix} H \\ H \end{smallmatrix} O$, acetic acid is formed from it by the action of chloride of othyl C_2H_3OCl , which forms $\begin{smallmatrix} C_2H_3O \\ H \end{smallmatrix} O + HCl$, *i.e.* hydrated acetic acid and hydrochloric acid. If a second atom of chloride of othyl is made to act upon this acetic acid, or better upon the acetate of potash $\begin{smallmatrix} C_2H_3O \\ K \end{smallmatrix} O$, we get, besides chloride of potassium, a compound $\begin{smallmatrix} C_2H_3O \\ C_2H_3O \end{smallmatrix} O$ which when compared to the original type, may be considered as water having both its atoms of hydrogen replaced by the radical othyl, C_2H_3O . This compound is the anhydrous acetic acid which might be called the acetate of othyl, inasmuch as that radical has, in the formation of the compound,

taken the place of the basic potassium in the acetate of potash.

In like manner, the anhydrous benzoic acid $\begin{smallmatrix} \text{C}_7\text{H}_5\text{O} \\ \text{C}_7\text{H}_5\text{O} \end{smallmatrix} \text{O}$ was made by the action of the chloride of benzoil $\text{C}_7\text{H}_5\text{OCl}$ on the benzoate of potash. It is a crystalline body, perfectly neutral to test paper, scarcely soluble in water, readily soluble in alcohol and ether. On continued boiling with water, it is converted into hydrated benzoic acid, one atom of the anhydride with one atom of water forming two atoms of the hydrated acid by an interchange of hydrogen and benzoil. Besides several of these anhydrous acids, Gerhardt has prepared some intermediate acids, analogous to the intermediate ethers, by combining two different radicals in the same group. Thus chloride of benzoil with cuminate of potash $\begin{smallmatrix} \text{C}_{10}\text{H}_{11}\text{O} \\ \text{K} \end{smallmatrix} \text{O}$ formed cuminate of benzoil or benzocuminic acid $\begin{smallmatrix} \text{C}_{10}\text{H}_{11}\text{O} \\ \text{C}_7\text{H}_5\text{O} \end{smallmatrix} \text{O}$; and in like manner, several other intermediate acids were prepared.

In conclusion, to this very brief exposition of this important series of discoveries, the Lecturer alluded to a feature of the development of the human mind in scientific research, which is strikingly illustrated by the substance and form of these results, and of which instances are probably to be found in the history of many others. The explanation of the above reactions consists in a combination of two modes of reasoning, which were developed by different schools, and for many years were used independently of one another. Gerhardt, to whose researches and writings some important steps in the doctrine of types are owing, formerly believed the truths which he saw

from that point of view to be incompatible with the idea of radicals, but he now joins those chemists who find in each of these notions a necessary and most natural complement to the other.

May we not hope that such may be the result in other cases of difference of opinion on scientific questions, which the progress of knowledge will shew to have been owing to the incompleteness and one-sidedness of each view rather than to any thing absolutely erroneous in either?

NOTE ON THE DECOMPOSITION OF SULPHURIC ACID BY PENTACHLORIDE OF PHOSPHORUS.*

CHEMISTS have long been aware of the fact that some acids unite with bases in one proportion only, others in two or more proportions. Thus a given quantity of nitric acid forms with what is termed its equivalent of potash, a definite nitrate of potash; if less than this equivalent quantity of potash were added to the nitric acid, the product would be a mechanical mixture of the same nitrate of potash with uncombined nitric acid; if more

* [From *Proceedings of the Royal Society of London*, vol. vii. (1856), pp. 11-15.]

than the equivalent of potash were added, the excess of alkali would remain uncombined. Sulphuric acid, on the other hand, is capable of forming two compounds with potash, and it depends upon the proportions in which the two substances are brought together whether the neutral or acid sulphate is formed.

The number of compounds which an acid forms with one base is now considered as indicating its atomic weight. The weights of sulphuric and nitric acids which are respectively susceptible of neutralizing the same quantity of potash are termed *equivalent*, but these are by no means the same as their *atomic* weights. Sixty-three parts of nitric acid (nitrate of water) contains the same quantity of hydrogen as forty-five parts of sulphuric acid, and when they are neutralized by potash the whole of this hydrogen is removed and replaced by potassium; and if neither of the acids could combine in any other proportion with potash, their atomic weights would be the same as their equivalent weights. But sulphuric acid also forms a potash compound in which half of its hydrogen is replaced by potassium, the other half remaining in the compound, whereas the smallest particles of nitric acid either exchange the whole or none of their hydrogen for potassium.

This fact is expressed in the simplest possible manner by the statement that the smallest indivisible particles of sulphuric acid contain two atoms of hydrogen, whilst those of nitric acid only contain one. Thus it is, that whereas the equivalent weights of the two acids are the quantities which contain the same amount of basic hydrogen, their atomic weights must be in the proportion of two equi-

valents of sulphuric to one of nitric acid. The simplest expression for an atom of nitric acid being empirically NO_3H , we shall accordingly represent an atom of sulphuric acid by the formula SO_4H_2 . In like manner, an atom of common phosphoric acid, being tribasic, is expressed empirically by the formula PO_4H_3 . The labours of Messrs. Laurent and Gerhardt greatly contributed to the establishment of these results, which are uncontroverted.

We have hitherto been accustomed to resort very freely to imaginary distinctions of form and arrangement of matter to explain the differences of properties ; but of late years an opposite tendency has arisen, and chemists have felt the necessity of reducing their language and ideas to simpler and more consistent forms. This necessity was first felt in the most complex, *i. e.* the so-called organic part of chemistry. But the simplifications thus introduced have proved to be equally applicable to the inorganic part of the science ; and their introduction is calculated to disengage, for the consideration of substantial differences of composition, the attention which has hitherto been absorbed by imaginary distinctions of form. Being unable to express the constitution of compounds without some formal artifice, we shall be able to see and compare their substantial differences most easily when all unnecessary variations of those formal artifices are eliminated. The success of this operation of course depends on our finding one form sufficiently general to replace the special and limited forms now employed.

In some papers published in the Journal of the Chemical Society two or three years ago, I endeavoured to show that the constitution of salts may be reduced to the type of water ; that acids

and bases being, truly, acid salts and basic salts, are perfectly conformable to the same principle; and that, amongst other things, the difference between monobasic and bibasic acids, &c. admits of a simple and easy explanation by it. The leading propositions in those papers have been adopted by several eminent chemists in this country and in France; and M. Gerhardt speedily enriched science with a series of brilliant and striking illustrations of their truth. As regards the constitution of bibasic acids, M. Gerhardt's results were, however, at variance with that theory; and he was led to represent them by formulæ equally inconsistent with his own previous views on the subject. I believe that this discrepancy is satisfactorily removed by the facts I have the honour of submitting to the consideration of the Society.

An atom of nitric acid, being eminently monobasic, is, as we have already shown, represented in the monobasic type $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{O}$ by the formula $\begin{smallmatrix} (\text{NO}_2) \\ \text{H} \end{smallmatrix} \text{O}$, in which peroxide of nitrogen (NO_2) replaces one atom of hydrogen. In like manner, hydrate of potash $\begin{pmatrix} \text{H} \\ \text{K} \end{pmatrix} \text{O}$ is obtained by replacing one atom of hydrogen in the type by its equivalent of potassium; and nitrate of potash $\begin{pmatrix} \text{NO}_2 \\ \text{K} \end{pmatrix} \text{O}$ by a simultaneous substitution of *one* atom of hydrogen by peroxide of nitrogen, the *other* by potassium. Sulphuric acid is formed from two atoms of water $\begin{smallmatrix} \text{H} & \text{O} \\ \text{H} & \text{H} \\ \text{H} & \text{O} \\ \text{H} & \text{H} \end{smallmatrix}$; one of hydrogen from each is removed, and the two

replaced by the indivisible radical SO_2 . The series

Sulphuric acid.	Acid sulphate of potash.	Neutral sulphate of potash.
$\begin{array}{c} \text{H}\text{O} \\ \text{SO}_2 \\ \text{H}\text{O} \end{array} ;$	$\begin{array}{c} \text{H}\text{O} \\ \text{SO}_2 \\ \text{K}\text{O} \end{array} ,$	$\begin{array}{c} \text{K}\text{O} \\ \text{SO}_2 \\ \text{K}\text{O} \end{array}$

explains itself.

Chemists have long known how to remove the basylous constituents H, K, &c. of these salts, and to replace them by others. But it is only recently that they have learnt to remove the chlorous radicals SO_2 , NO_2 , &c. in a similar manner. To obtain the chloride of potassium from its sulphate, it is sufficient to bring the latter into liquid contact with chloride of barium ; but the same reagent would be powerless for the preparation of the chlorides of the radicals SO_2 or NO_2 .

M. Cahours has shown us a reagent (the pentachloride of phosphorus) which is capable of forming from a great number of monobasic acids the chlorides of the acid radicals. Whilst extending our knowledge of the action of the body on monobasic and organic acids, and preparing numerous compounds of their radicals with one atom of chlorine, M. Gerhardt examined also the nature of its action upon bibasic acids and their compounds ; and states that it consists of two successive phases, first, the liberation of the anhydrous acid, secondly, the substitution of two atoms of chlorine for one of oxygen in that anhydrous acid. These facts, if correct, would be unfavourable to the above view of the constitution of sulphuric and the other bibasic acids ; and M. Gerhardt adopted accordingly the old formulæ, representing in their composition an atom of water ready-formed, $\text{SO}_3 \text{H}_2 \text{O}$.

Confining my remarks for the present to the case

of sulphuric acid, whose decomposition is doubtless typical of that of other bibasic acids, I may state as the result of numerous experiments with the most varied proportions of pentachloride and acid, performed on a scale of considerable magnitude, that the first action of the pentachloride consists in removing one atom of hydrogen and one of oxygen (empirically peroxide of hydrogen) from the acid, putting in an atom of chlorine in their place, and forming the

compound $\text{SO}_2 \overset{\text{H O}}{\underset{\text{Cl}}{}} \text{}$, which is strictly intermediate be-

tween the hydrated acid and the final product SO_2Cl_2 formed by a repetition of the same process of substitution of chlorine for peroxide of hydrogen. The existence and formation of this body, which we may call chloro-hydrated sulphuric acid, furnishes the most direct evidence of the truth of the notion, that the bibasic character of sulphuric acid is owing to the fact of one atom of its radical SO_2 replacing or (to use the customary expression) being equivalent to two atoms of hydrogen. Had this radical been divisible like an equivalent quantity of a monobasic acid, we should have obtained a *mixture*, not a *compound* of the chloride with the hydrate,—or, at least, the products of decomposition of that mixture.

Chloro-hydrated sulphuric acid boils at 145° Cent., distilling without decomposition. The intensity of its action upon water varies according to the manner in which the two bodies are brought together. When poured rapidly into a large quantity of cold water, a portion of it sinks to the bottom, and only gradually dissolves as a mixture of hydrochloric and sulphuric acids. When a small quantity of water is added to the compound, the same decomposition takes place

with explosive violence. The acid dissolves chloride of sodium on the application of a gentle heat with evolution of hydrochloric acid, giving rise to a com-

pound of the formula $\text{SO}_2 \overset{\text{Na}}{\text{O}} \underset{\text{Cl}}{\text{Cl}}$. When poured upon

pieces of melted nitre at the atmospheric temperature, an effervescence takes place with evolution of a colourless vapour which possesses in a striking degree the odour of aqua regia. This vapour may be dissolved in various liquids, and when decomposed by water, yields nitric and hydrochloric acids. It is doubtless chloro-nitric acid, NO_2Cl . In like manner the chlorides of other inorganic acid radicals may be obtained, as from chlorates, perchlorates, sulphites, &c., but of these and other reactions I beg leave to defer any further account until the experiments now in hand are more advanced.

From the general resemblance of properties and identity of boiling-point of the chloro-hydrate with a compound discovered by Rose, and described by that eminent chemist as possessing empirically the composition $\text{S}_2\text{O}_5\text{Cl}_2$, I was led to suspect that the two might in reality be identical, which of course would require the addition of the elements of water to Rose's formula, and several experiments I have performed afford strong confirmation of that identity. The same compound is obtained by the action of dry hydrochloric acid on anhydrous sulphuric acid; and finally, I may mention that Mr. Railton obtained a small quantity of the same substance some weeks ago in my laboratory by the action of platinum-black at a high temperature on an imperfectly dried mixture of chlorine and sulphurous acid.

As regards the successive transformations effected

in the pentachloride, I have observed the formation of Wurtz's oxychloride (the tribasic chloro-phosphoric acid (POCl_3)), and also of a compound boiling above 145° , probably PO_2Cl . Hydrated phosphoric acid is always found unless the amount of pentachloride added is very great.

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